Study metal dusting phenomenon in simulated process environments

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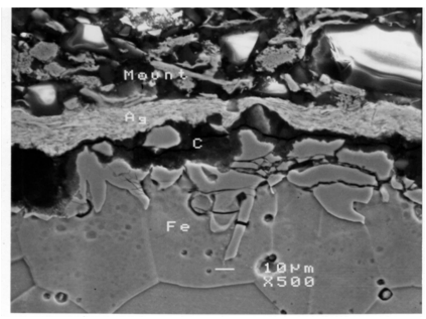
Introduction

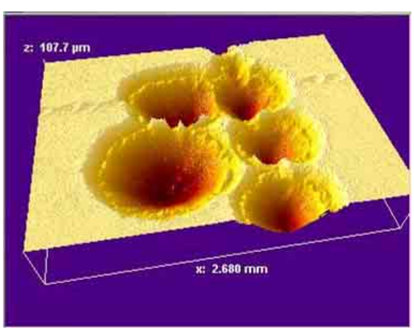
Metal dusting is a metal loss process that occurs in hot reactive gases

The prerequisite for metal dusting is that carbon activity in the gas phase has to be >>1

Metal ends up as fine powder



Pitting and crevice attack are common forms



Environments conducive to metal dusting are reformers of different types (e.g., hydrogen, methanol, ammonia, etc.) syngas systems and others

Goal

- Evaluate the mechanism(s) for the metal dusting phenomenon from a fundamental scientific base involving laboratory research in simulated process environments.
- Establish the key parameters responsible for metal dusting initiation and propagation.
- Experimentally determine the role of system pressure on metal dusting initiation and propagation.
- Evaluate the corrosion performance of commercial alloys and coatings in simulated metal dusting environments.
- Develop/modify alloys and coatings that resist metal dusting and explore process fix to mitigate corrosion.

Challenge

No alloys can resist metal dusting corrosion in long term.
Need to search for a solution to solve metal dusting corrosion in various industry environments.

Benefits

- 475 billion BTU per day could be saved
- Fewer maintenance shutdowns
- Increased productivity
- Reduction of $50 thousand per plant per year in operating costs
- Saving of 220-290 million annually in the hydrogen industry

Chemical Industry Participants

- Materials Technology Institute of the Chemical Process Industries
- Air Products and Chemicals Inc.
- ExxonMobil Chemical Company
- DuPont Chemical Company
- Allied Signal (may rejoin program as Honeywell)
- Haynes International
- AvestaPolarit
- Sandvik Steel
- Duraloy Technologies, Inc.
- Special Metals
- Krupp VDM
- Schmidt & Clemens
- Alon Surface Technologies
- MetalTek International
- Spectrum Metals (Rolled Alloys)

FY05 Activities

- Build a large high pressure test system with three temperature zones
- Establish a system to measure pit depth.
- Develop pre-pitting technology to accelerate the study on the steady state of metal dusting.
- Performance high pressure test on alloys.
- Test Ni-base alloys in various metal dusting environments.
- Develop new alloys to resist metal dusting corrosion

Alloys for metal dusting experiments

Iron-base Alloys

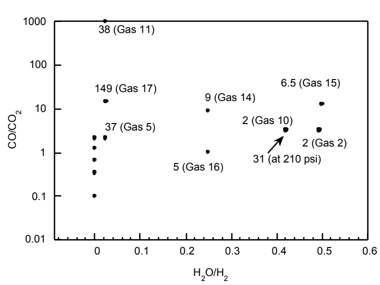
Alloy	Cr	Ni	Si	Mo	Al	Fe	Other
T22	2.3	-	0.5	1.0	-	Bal	-
T91	8.6	0.1	0.4	1.0	-	Bal	N 0.05, Nb 0.07, V 0.2
153MA	18.4	9.5	1.4	0.2	-	Bal	N 0.15, Ce 0.04
253MA	20.9	10.9	1.6	0.3	-	Bal	N 0.19, Ce 0.04
353MA	24.4	34.7	1.3	0.1	-	Bal	N 0.18, Ce 0.03
321L	17.4	9.3	0.5	-	-	Bal	N 0.02, Ti 0.3
310	25.5	19.5	0.7	-	-	Bal	-
800	20.1	31.7	0.2	0.3	0.4	Bal	Ti 0.31
803	25.6	36.6	0.7	0.2	0.5	34.6	Ti 0.6
38815	13.9	15.3	5.8	1.0	0.13	Bal	-
MA956	20.0	-	-	-	4.5	Bal	Ti 0.5, Y_2O_3 0.6
321	17.3	10.3	0.4	-	-	Bal	Ti 0.4, N 0.01
APMT	21.7	-	0.6	2.8	4.9	Bal	
4C54	26.7	0.3	0.5	-	-	Bal	N 0.19

Nickel-base Alloys

Alloy	Cr	Ni	Si	Mo	Al	Fe	Other
600	154	Bal	0.1	-	-	9.7	-
601	219	Bal	0.2	0.1	1.4	145	Ti 0.3,Nb0.1
690	272	Bal	0.1	0.1	0.2	102	Ti 0.3
617	216	536	0.1	9.5	1.2	0.9	Co12.5,Ti 0.3
625	215	Bal	0.3	9.0	0.2	2.5	Nb3.7,Ti 0.2
602CA	251	Bal	0.1	-	2.3	9.3	Ti 0.13,Zr 0.19, Y 009
214	159	Bal	0.1	0.5	3.7	2.5	Zr 0.01, Y 0006
230	217	Bal	0.4	1.4	0.3	1.2	W14,La 0.015
45TM	274	464	2.7	-	-	267	RE 0.07
HR160	280	Bal	2.8	0.1	0.2	4.0	Co30.0
693	289	Bal	0.04	0.13	3.3	5.9	Ti 0.4,Nb0.7,Zr 0.03

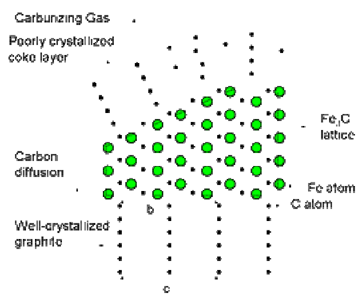
Experimental Details

Primary variables: Temperature, Pressure, Time, Alloy chemistry, Gas chemistry
Materials: Fe- and Ni-base alloys, coatings
Gases: Mixtures of CO, CO2, CH4, H2, and H2O
Test Pressures: 1 - 40.8 atm (14.7 - 600 psi)
Test temperatures: 900 - 1300°F (482 - 704°C)
Test times: 100 h initially; long term 5000-6000 h
Post test evaluation:
- Weight change
- Optical and Scanning electron microscopy
- Energy dispersive X-ray analysis
- X-ray diffraction (carbon and alloys)
- Raman analysis (carbon and alloys)

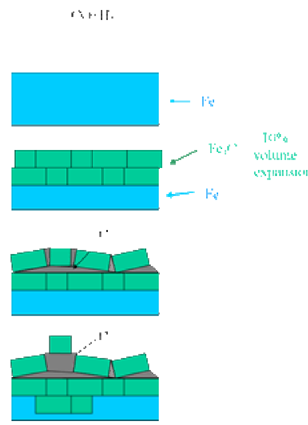


Gas Chemistry and carbon Activity in Experimental Runs

Mechanism of metal dusting

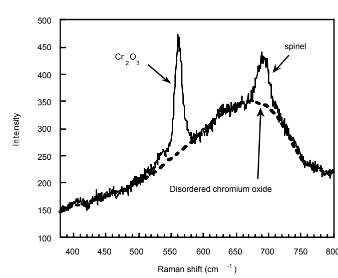


Schematic of Coke Crystallization

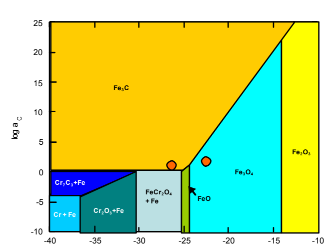


Schematic of Metal Dusting Attack

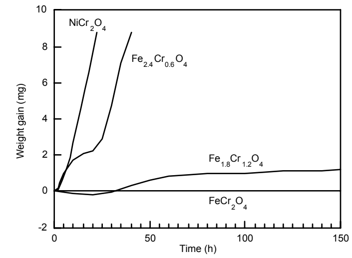
Effect of Phase Composition on Metal Dusting



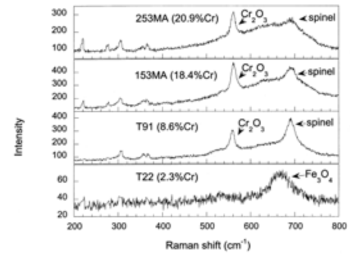
Phases Present in Oxide Scale Developed on 153MA



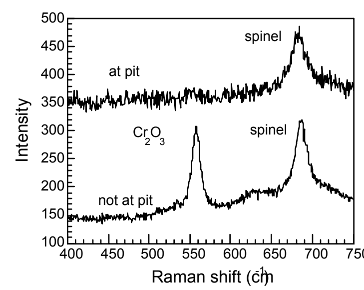
Fe-Cr-O-C Thermodynamic Stability Diagram



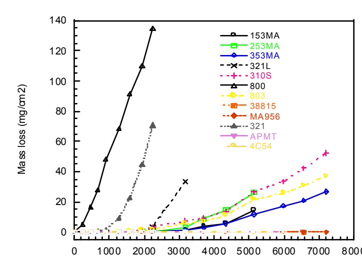
Weight change for different spinels in MD environment. Stability of sipnel with higher Fe content is worse



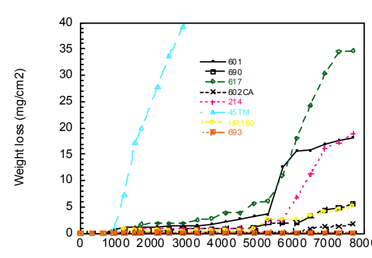
Spinel phase increases with increasing iron content in alloys



Raman Spectra of Alloy 800 after 1280 h in MD Environment

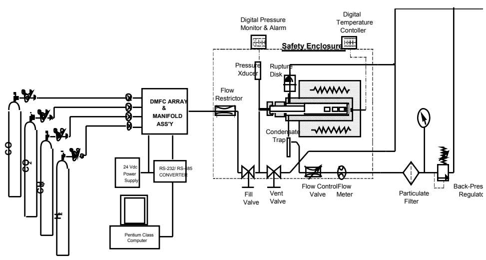


Metal Loss for Fe-base Alloys, 1 atm at 593°C, a_C = 38

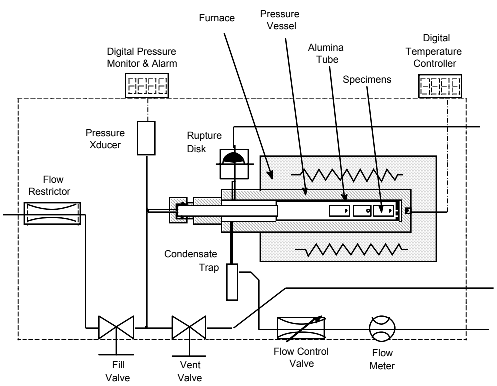


Metal Loss for Ni-base Alloys, 210 psi at 593°C, a_C = 30

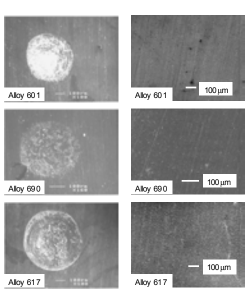
Effect of system pressure



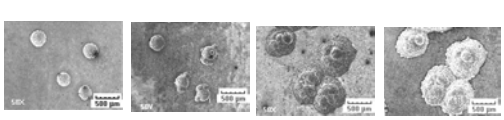
System for High Pressure Tests



Details of High Pressure Test System

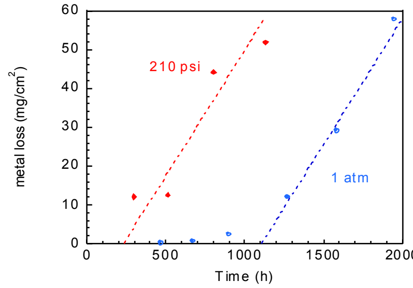


SEM micrograph of Ni-base alloys.
Left: exposed at 15 atm and 593°C for 160 h, metal dusting pits were observed.
Right: exposed at 1 atm and 593°C for 240 h, surfaces of alloys are smooth, and no metal dusting pits appeared.

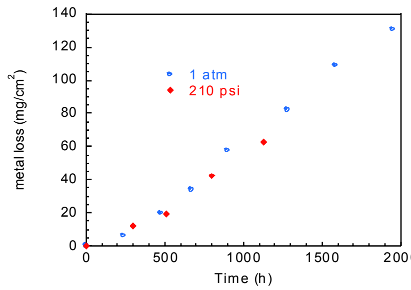


2900 h 4100 h 7700h 9300h

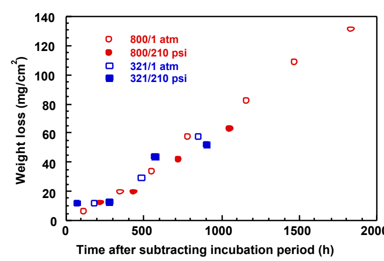
Sizes of pits on alloy 617 increase with time at 210 psi and 593°C



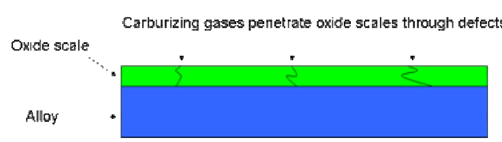
Metal loss of Alloy 321 at 593ºC



Metal loss of Alloy 800 at 593ºC



Metal loss of Alloy 800 and 321 at 593ºC



High pressure leads to high chemical potential for carburizing gas to penetrate through defects in oxide scale on surface of alloys

Conclusion

- The mechanism for metal dusting is a process of catalytic crystallization of carbon with participation by iron and nickel
- Raman spectra show the existence of spinel, Cr_2O_3, and disordered chromium oxide in the scale grown on Fe-Cr alloys. All three phases act as protective layers to prevent alloys from metal dusting corrosion. However, the spinel phase is not as stable as Cr_2O_3. It could be reduced, and metal dusting corrosion would initiate from the reduced defects.
- Alloy composition, oxygen partial pressure in the gas mixture, and alloy pre-treatment can affect the phase composition in oxide scales.
- High system pressure reduces incubation time, but does not change metal dusting rate if carbon activity is maintained same.

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